PATENT SPECIFICATION

DRAWINGS ATTACHED

COMPLETE SPECIFICATION

Process for improving Kerosenes and Diesel Fuels

We, Esso Research and Engineering Company, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns a novel process for upgrading petroleum fractions boiling in the kerosene and diesel fuel boiling ranges, i.e. 300 to 650°F. The invention is of particular application for processing of virgin stocks but is also applicable and of value in improving catalytically cracked stocks boiling in the general range of 430° to 650°F. As applied to kerosenes, the invention is of particular utility in providing an attractive means for improving the smoke point of such stocks. As applied to diesel fuels, the invention serves to improve the cetane number of these fuels.

In the case of diesel fuels and kerosenes, the ignition characteristics and the burning characteristics respectively are of particular importance from the viewpoint of product quality. These characteristics are often controlling in refining operations necessitating specific techniques for improving these properties of these stocks. Burning characteristics of a kerosene may be measured by smoke point tests which can readily be carried out by determining the height of flame obtainable at incipient smoking, with the aim being to obtain kerosenes having the highest value of smoke point. The ignition characteristics of diesel fuels which are pertinent to this invention can be determined by cetane number inspections. These properties of the fuels identified are each dependent on the aromatic content of the fuel. Thus, both kerosene and diesel fuels, which are highly aromatic, are normally deficient in the identified characteristics. To a lesser degree, these characteristics are also related to and effected by the naphthene content of the fuel. For these reasons, the present invention is particularly applicable to petroleum fractions boiling within a boiling range of 300—650°F which contain at least 10% by weight and up to 50% by weight of aromatic hydrocarbons and which have a naphthene ring content of less than 30%. More specifically, the invention is of particular application to virgin kerosenes boiling to the range of 300—500°F, and to virgin or cracked diesel fuels boiling in the range of 300—625°F.

In order to improve the burning properties of these fuels, it is necessary to selectively hydrogenate the aromatic compounds present. It is, of course, preferable to obtain complete conversion of all aromatic hydrocarbons, although conversions above about 90%, and particularly above 98% are effective for substantially upgrading these fuels.

In order to establish the nature and advantages of this invention, reference will be made to some of the critical features which must be observed in upgrading kerosenes and diesel fuels As a starting point, consideration will be directed to the performance of possible catalysts for obtaining the hydrogenation of aromatic hydrocarbons which is required for the purposes of the invention. As a first step of this study, a variety of hydrogenation catalysts which have proved commercially superior in other types of hydrogenation were evaluated for activity in hydrogenating the aromatic nucleus. In these tests, low sulfur kerosene from Sweden crude was employed. Standard hydrogenation conditions for each of the catalysts were selected, namely a pressure of 800psig., 600°F., and a throughput of 4 V/Hr./V.

A commercial cobalt molybdate on alumina catalyst of the nature now used in commercial hydrofining operations was first tested.

[Price 3s. 6d.]

While this catalyst has excellent activity for conversion of sulfur combinations to provide low sulfur treated stocks, this catalyst was found to have no activity for the conversion of aromatics under the conditions of this test. At the other extreme of activity among the catalysts tested, it was found that a commercially available nickel catalyst comprising 43% by wt. of nickel supported on Kieselguhr was extremely active for aromatic conversion. None of the other catalysts tested were found to have an activity for aromatic hydrogenation even approaching that of this nickel catalyst. For example, a platinum on alumina catalyst of the type used in commercial reforming operations was found to have only about 1/10 the activity of the nickel catalyst in this service. Again, for example, a commercial rhodium on alumina catalyst was found to have an activity of nil.

It is apparent from these results that upgrading of kerosenes and diesel fuels by hydrogenation requires a specific type of hydrogenation requires a specific type of

catalytic activity which is unique in character and is not possessed by most hydrogenation 25 catalysts. A nickel catalyst preferably supported on Kieselguhr or alternatively carried on other supports such as alumina is unexpectedly superior to other catalysts and, in fact, possesses unique properties for the 30 objectives of this invention.

In attempting to use the nickel catalyst for upgrading kerosenes and diesel fuels so as to obtain the benefit of the aromatic conversion activity of this catalyst, the following results 35 are representative. In these tests, the kerosene and diesel fuel employed were derived from a Tia Juana crude oil and a catalyst consisting of 43% by wt. of nickel supported on Kieselguhr was employed. The hydro- 40 genation conditions used were a temperature of 550°F., a pressure of 800 psig, a throughput of 1V/Hr./V and a hydrogen rate of 1500 standard cubic feet per barrel. The results are summarized in the following table: 45

TABLE I

Feed Stock	Kerosene		Auto Diesel Fuel	
Inspections	Feed	Product	Feed	Product
Sulfur, wt. %	0.3	0.09	0.72	
Gravity, °API	41.6	45.0	36.0	40.6
Aniline Point, °F.	141	163	153	174
Smoke Point, mm.	20	33	—	—
Cetane No.	—	—	46	53
Cataylst Life				
Oil Processed (1) Vol. Oil/Vol. Cat.		33		6

(1) Before catalyst deactivation became appreciable.

In comparing the inspections for both the diesel and kerosene feed and products, it will be noted that substantial improvements in cetane number and smoke point respectively of these products were obtained. However, referring to the last line of the table, the data show the volume of oil processed per volume of catalyst when catalyst deactivation became appreciable. It will be observed in the case of kerosene, that only 33 volumes of oil per volume of catalyst could be processed before appreciable catalyst deactivation occurred. In the case of the diesel fuel, extremely rapid catalyst deactivation resulted so that only 6 volumes of oil per volume of catalyst could be

processed. It is apparent from this data that the catalyst life involved was far too short to permit commercial utilization of such a process. 65

In an extensive study of this problem of catalyst deactivation, it was found that this is a peculiar function of the sulfur content of the system affected by the proportion of hydrogen present during hydrogenation. In a first study 70 of this matter, it was found in treating feed stocks of different sulfur levels that the rate of catalyst deactivation could be plotted linearly with respect to the sulfur content of the feed stock treated. Such data suggested 75 that by desulfurizing feed stocks completely,

this mechanism of catalyst deactivation could be avoided. However, while it is commercially feasible to reduce the sulfur content of petroleum fractions to low levels, it is not ordinarily commercially feasible to completely eliminate all sulfur constituents. This data therefore indicated that catalyst deactivation could not be avoided but could only be minimized in practical commercial applications.

Further studies however, showed that below critical values of sulfur content, the effects of sulfur in deactivating a nickel catalyst in the process of this invention could be offset by employing critically high ratios of hydrogen partial pressure. It is theoretically felt that this peculiar phenomenon is represented by the following reactions.

Feed Sulfur + Ni(catalyst)→ Ni$_3$S$_2$ + Hydrocarbon. Because of the hydrogen treat gas, some of the Ni$_3$S$_2$ is converted back to nickel by the competing reaction.

Ni$_3$S$_2$ + 2H$_2$ → 3 Ni + 2H$_2$S
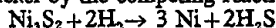
Recognizing the effect of these reactions, equilibrium data were established to determine the hydrogen rates required to prevent formation of nickel sulfide. These determinations establish the following allowable limits of feed sulfur content so as to prevent conversion of nickel sulfide.

TABLE II

Temp. °F.	500		600		700	
H$_2$ Rate, SCF/B	1000	5000	1000	5000	1000	5000
Feed Sulfur, Wt. % (1)	0.0005	0.0024	0.001	0.005	0.002	0.009

Based on these principles, it is the particular feature of this invention to employ hydrogenation gas rates in excess of 2,000 standard cubic feet of hydrogen per barrel of feed. Gas rates higher than this value are preferable and are commercially feasible up to rates of about 10,000 standard cubic feet per barrel. With such gas rates, as indicated above, catalyst deactivation can be completely suppressed provided sulfur content of the feed stock used is maintained at not more than 20 parts per million of sulfur. Obtaining sulfur contents of this magnitude is commercially feasible as opposed to the difficulty or impracticability of obtaining complete desulfurization. The hydrogen gas may be recycled to the process, but H$_2$S is preferably first removed therefrom.

As set forth therefore, the present invention comprises a process for upgrading petroleum fractions containing aromatic and sulfur compounds and boiling in the range of 300—650°F. which comprises desulfurising said fractions in a first stage to a sulfur level of not more than 20 parts per million by weight and thereafter hydrogenating said fractions over a nickel catalyst maintaining hydrogen rates in excess of 2000 standard cubic feet per barrel. Under the conditions of this invention, attractive product quality improvements are obtained at pressures in the range of 200 to 800 p.s.i.g, temperatures in the range of 500—550°F, and feed rates of 1—5 V/Hr./V. More specifically, it is particularly preferred to process kerosenes at pressure of 300—400 p.s.i.g, and at the particular throughputs of 2—4 V/Hr./V. at the temperatures indicated. Similarly, it is preferred to process diesel fuels at pressures of 400—800 p.s.i.g., and at the particular rates of 1 to 1.5 V/Hr./V. at the temperatures indicated.

The catalyst preferably used for the desulphurization process is of the cobalt molybdate type. Such catalysts include what are probably actual complexes of cobalt and molybdenum which have been identified as cobalt molybdate but include as well the use of mixed oxides or sulfides of cobalt and molybdenum. These catalysts are supported on a suitable absorptive support which is preferably alumina and some 5—15% by weight of the catalytic agent is ordinarily employed on alumina. Use of this catalyst for feed stock desulfurization in the practice of this invention is particularly effective in view of the desulfurization and aromatic conversion capacities of these catalysts. Although the cobalt molybdate desulphurization treatment is ineffective in eliminating aromatic hydrocarbons, as single ring aromatic hydrocarbons are not hydrogenated under these conditions, it has been found that the cobalt molybdate does serve to break down or partially hydrogenate multiple ring aromatic hydrocarbons. Thus the use of cobalt molybdate as catalyst in the desulphurizaiton step of the present invention, resulting in the consequent conversion of multiple ring aromatic hydrocarbons, is of particular utility.

Preferred conditions for the desulphurization step of the invention require use of a temperature of about 600° to 800°F., a pressure of about 200 to 800 p.s.i.g, and a feed rate of

at least 1 V/Hr.V. It will be observed from these process conditions that higher temperatures are required for the cobalt molybdate step of the process than employed in the nickel hydrogenation step of the process. Furthermore, contrary to the necessity for avoiding the presence of hydrogen sulfide during the nickel hydrogenation, hydrogen sulfide is required to be present during desulfurization with cobalt molybdate so as to maintain catalytic activity. These and other differences between the two treating stages employed again impose specific problems in combining these operations.

Referring now to the accompanying drawings:

Figure 1 diagrammatically illustrates a preferred flow plan for the practice of this invention, particularly for upgrading of diesel fuel or for smaller sized commercial plants.

Figure 2 diagrammitcally illustrates a preferred flow plan for the practice of this invention of particular application for large scale commercial units.

In each of these flow plans, particular provisions are made to carry out the principles of this invention which have been identified and to obtain additional treating improvements. In this connection, for example, the flow plans permit maintaining the two hydrogenation stages at the different conditions required even through employing a common recycle hydrogen stream and utilizing only a single furnace. These and other features will be appreciated from a description of the drawings.

Referring first to Figure 1, a single hydrogenation reactor is employed identified by numeral 2, in which a nickel catalyst may be positioned in the lower half of the reactor with a cobalt molybdate catalyst in the upper half of the reactor. These distinct catalyst beds may be separated by suitable perforated grids so as to accommodate a heat exchanger 3 at an intermediate portion of reactor 2 between the beds of catalyst. Employing this reactor, the feed stock to be treated is brought into the system through line 4 and is passed in heat exchange with the hydrogenation products in heat exchanger 5. This preheated oil feed is then passed through heat exchanger 3 intermediate between the two catalyst beds and is then passed through a furnace 6 so as to be brought to a temperature of 600° to 800°F. The heated feed is then brought into an upper portion of reactor 2 spaced below the top of the cobalt molybdate catalyst bed. Hydrogen is brought into the bottom of reactor 2 through make-up hydrogen inlet line 10 and through line 11. This hydrogen passes upwardly through the catalyst from the bottom of the reactor for eventual removal through line 12 at the top of reactor.

Lighter constituents of oil feed introduced to the top of the reactor through line 4 are vaporized and are passed upwardly through the cobalt molybdate catalyst in the presence of hydrogen for removal through line 12. Heavier liquid constituents of oil feed pass downwardly through the cobalt molybdate catalyst to the zone provided by heat exchanger 3. Here the oil is dropped in temperature to a temperature below 600°F., preferably 500—550°F, prior to contact with the nickel, catalyst and hydrogen in the lower portion of the reactor. The treated oil is then removed from the bottom of the reactor through line 13.

Hydrogen and lighter oil constituents removed from reactor 2 through line 12 are passed through heat exchanger 14 to a separator 15. In separator 15, separation of hydrogen and the oil is accomplished permitting removal of the oil constituents from the bottom of separator 15 through line 16. A portion of this oil is recycled to the system through line 17 and heat exchanger 14 while a portion of this oil may be removed from the system through line 18 for blending with the treated oil of line 13.

Recycle hydrogen gas removed from the upper portion of separator 15 through line 19 is treated to remove hydrogen sulfide in zone 20. Hydrogen sulfide removal may be accomplished by conventional means including caustic washing or scrubbing with an amine solution such as diethanol amine. This H_2S free hydrogen is then compressed in compressor 21, blended with the light oil recycle of line 17 and passed back to reactor 2 through line 11.

It will be observed that in this processing technique all requisites of the completely different processing using the nickel and cobalt molybdate catalysts are obtained even though these processes are provided in an integral fashion. Thus, for example, hydrogen present for hydrogenation of oil in the presence of nickel catalysts is devoid of H_2S while H_2S generated by the nickel hydrogenation is availabale during desulphurisation in the cobalt molybdate section of the reactor. Again, for example, the different temperature conditions required in the two hydrogen stages are maintained while employing a single heating furnace.

In Figure 2 a similar processing technique is illustrated which embodies the same features of the system of Figure 1 but provides for a separation of the cobalt molybdate and nickel catalyst bed. In the system of Figure, 2 oil feed is brought into the system through line 30 and is pre-heated in heat exchanger 31 by heat exchange with hydrogenated products. The oil feed is then passed to furnace 32 through line 30 and may be brought into furnace 32 in admixture with recycle hydrogen gas of line 33 derived from the nickel hydrogenation zone 34. The oil and recycle hydrogen heated to a temperature of 600° to

800°F. is then passed through line 35 for de-
sulpuhrization in zone 36 containing cobalt
molybdate catalyst. The desulfurized oil
together with hydrogen is then passed through
line 37 and heat exchanger 38 to separator-
stripper zone 39. Fresh hydrogen is
brought into the bottom of stripper zone
39 through line 40 so as to scrub
out hydrogen sulfide from the oil pro-
duct, which is removed from the bottom of
the separator through line 41. Hydrogen is
removed from the top of the separator
through line 42 for treatment to remove
hydrogen sulfide in zone 43. The hydrogen
sulfide-free hydrogen is then combined with
the oil of line 41 and is passed through heat
exchanger 38 and through line 45 to the
hydrogenation reactor 34 containing nickel
catalyst. By the heat exchange provisions in-
dicated, this stream will have a temperature
below 600°F, e.g. in the range of 500—550°F.

Hydrogenated oil and hydrogen is removed
from the bottom of zone 34 through line 47
and is passed to separator 48. The final
treated product is then removed from the
separator 48 through line 49 and recycle
hydrogen is removed through line 33 as
described.

Having described the nature and practice of
this invention, an example is given below to
show the utility of the invention. The
following two experiments have also been
carried out but are included in the specifica-
tion for comparitive purposes only.

EXPERIMENT I

A kerosene having the low surfur content
of 0.03 weight percent and boiling in the range
of 300—500°F. was subjected to hydro-
genation using a nickel catalyst in accordance
with the invention. The hydrogenation con-
ditions used and the treating conditions are
set forth in the table below.

TABLE III

Kerosene Hydrogenation for Smoke Point Improvement

Catalyst		43% Ni on Kieselguhr		
Conditions:				
Temperature, °F.		—— 600 ——		550
Pressure, psig		————— 800 —————		
Feed Rate, V/Hr./V		1.0	4.5	4.5
H₂ Rate, SCF/B (100% H₂)		2000	—— 1000 ——	
Inspections:	Feed			
Sulfur, Wt. %	0.03	———— 0.0004 ————		
Gravity, °API	42.5	45.4	45.3	45.6
Aniline Point, °F.	143	160	161.5	162
R.I. @ 20° F.	1.4512	1.4402	1.4402	1.4402
Smoke Point, mm.	22	34	34	33
Aromatics, Wt. % (1)	16.4	0	0	0
Diesel Index	61	73	73	73
Cetane Number	49	—	51	—

(1) Estimated from specific dispersion measurements.

It will be observed from this data that com-
plete saturation of the aromatic hydrocarbons
was obtained, serving to substantially improve
the smoke of the kerosene.

EXPERIMENT 2

A diesel fuel fraction derived from a catalytically cracked stock was desulfurized in a first stage hydrogenation treatment using cobalt molybdate catalyst. The desulfurized diesel fuel was then hydrogenated over a nickel catalyst in accordance with this invention. The feed stock inspections and the condition of treatment employed are set forth in Table IV.

TABLE IV

Hydrogenation of Mid-Continent Cycle Stock

Catalyst			$CoMoO_4$		43% Ni on Kieselguhr	
Temperature, °F.		650	700		——— 500 ———	
Pressure, psig		——— 800 ———			——— 800 ———	
Feed Rate, V/Hr./V		1.0	1.0		1	4
Gas Rate, SCF/B		——— 1500 ———			——— 2000 ———	
Inspections	Feed				Feed (1)	
Aniline Pt., °F.	134	138	140	141	171	147.9
Gravity, °API	31.6	33.6	33.6	34.9	39.3	36.1
Diesel Index	42.3	46.4	47.0	49	67	54
Cetane No.	42.2	43.9	—	45.5	55.3	46.4
Color, Saybolt	19TR	10—1/4TR	10—1/2TR	13—3/4TR	+30	+16
Sulfur	0.24	0.003	0.002	0.003	—	—

(1) Composite of product from the runs made over the $CoMoO_4$ catalyst

It will be observed from this data that the cetane number of the diesel fuel has been substantially improved and also the product color has been improved to a value of +30 Saybolt which is water-white.

As emphasised heretofore, an imoprtant feature of the invention is utilization of a feed stock containing less than 22 ppm of sulfur for conversion of aromatic hydrocarbons by hydrogenation over a nickel catalyst. As shown by the data given in the above two experiments, good initial hydrogenation results are obtainable at higher sulfur contents but catalyst life is short.

EXAMPLE

The following example, set forth in Table V, shows the practicability of obtaining extensive catalyst life by the principles of this invention. The example concerns hydrogenation of a diesel fuel boiling in the range of 300—625°F derived from a Tia Juana crude oil, employing first stage cobalt molybdate desulfurization to 20 ppm of sulfur and second stage nickel hydrogenation at hydrogen rates of 2000—2500 SCF/B.

TABLE V

Operating Conditions	Feed	First Stage	Second Stage
Catalyst		CoMoO$_4$ on Al$_2$O$_3$	Ni on Kieselguhr
Temperature, °F.		725	550
Pressure, p.s.i.g.		400	800
Feed Rate, V/Hr./V		1/2	1
Sulfur Wt. %	0.67	.002	—
Diesel Index	53	54	71
Cetane No.	46	—	54
Gravity, °API	35.6	37.8	40.8
Aniline Pt. °F.	150	144	174

The hydrogenation was continued for a period in excess of 500 hours without any indication of catalyst deactivation.

WHAT WE CLAIM IS:—

1. A process for ungrading petroleum fractions containing aromatic and sulfur compounds and boiling in the range of 300—650°F, which comprises desulfurizing said fractions in a first stage to a sulfur level of not more than 20 parts per million by weight and thereafter hydrogenating said fractions over a nickel catalyst maintaining hydrogen rates in excess of 2000 standard cubic feet per barrel.

2. The process as claimed in claim 1 in which the said first stage desulfurization is conducted at a temperature of 600—800°F, a pressure of about 200—800 p.s.i.g, and a feed rate of at least 1V/Hr./V employing a cobalt molybdate catalyst in the presence of hydrogen.

3. The process as claimed in claim 1 or claim 2 in which the said nickel hydrogenation step is conducted at a pressure of 200—800 p.s.i.g, a temperature of 500—550°F, and a feed rate of 1—5V/Hr./V.

4. The process as claimed in any of claims 1 to 3 wherein the petroleum fractions contain 10 to 50% of aromatic hydrocarbons and have a naphthene ring content of less than 30%.

5. The process as claimed in any of claims 1 to 4 wherein the hydrogen rate during the hydrogenation of the petroleum fractions is maintained in excess of 2000 and up to 10,000 SCF/B.

6. The process as claimed in any of claims 1 to 5 wherein the nickel catalyst is supported on Kieselguhr.

7. The process as claimed in any of claims 2 to 6 wherein the petroleum fractions to be treated are passed downwardly over a bed of cobalt molybdate catalyst and then over a bed of nickel catalyst and then over a bed of nickel catalyst counter-current to an upward flow of hydrogen serially through said catalyst beds in which the said fractions are heated to a temperature of about 600—800°F for passage over the cobalt molybdate catalyst and are cooled to 500—550°F. for passage over the nickel catalyst.

8. The process as claimed in claim 7 wherein hydrogen sulfide is removed from a recycle hydrogen gas stream withdrawn from the top of the cobalt molybdate catalyst bed and the hydrogen sulfide free hydrogen is recycled to the bottom of the nickel catalyst bed.
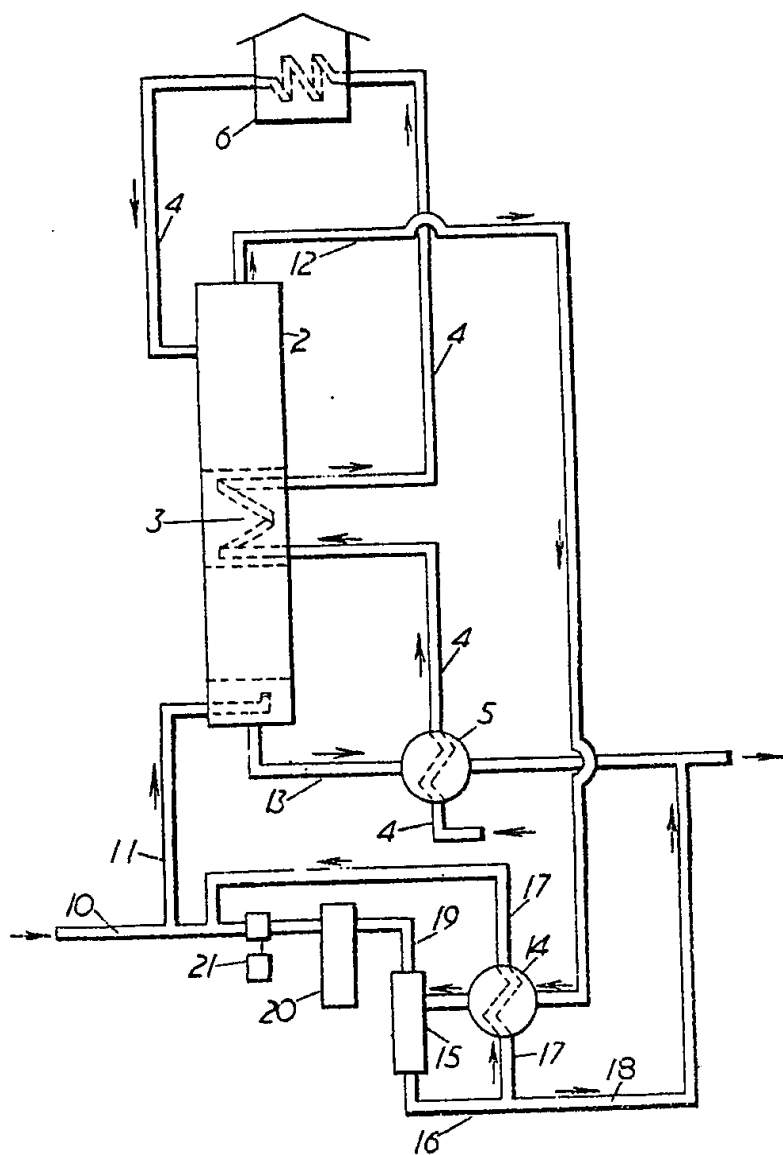
9. The process is claimed in claim 1 substantially as hereinbefore described in the Example.

10. The process as claimed in claim 1 substantially as hereinbefore described with reference to the accompanyg drawings.

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FIG. I.

FIG.2.

FIG.2.

FIG.1.